



Fabrication of iron disilicide (FeSi_2) thermoelectric generator by the tape casting method

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Abstract

The tape casting process has been applied to fabricate a thermoelectric generator consisting of a multi-layers of semiconducting FeSi_2 and insulating ceramic material layers. The production process of the thermoelectric generator is described in terms of powder production, green tapes manufacturing and lamination, pyrolysis, sintering and the annealing procedures for the laminated structure. A selection of some ceramic alloys which matched the required criteria to be used with the FeSi_2 semiconductor is also described. The performance of a thermoelectric generator made by the tape casting method, is compared to those made by conventional fabrication techniques. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Tape casting; Thermoelectric materials; Mechanical alloying; Multi-materials; Powder; Sintering

1. Introduction

The thermoelectric generator is a silent, reliable energy converter, which converts heat energy directly to electrical energy.

In the last 30 years of research in thermoelectricity, two fundamental problems were identified, the low efficiency of the thermoelectric materials and the high cost of fabricating the thermoelectric generator. The low efficiency of the thermoelectric materials, is a long-term research problem, its solution lies within a better understanding of solid state physics or even a radical rethinking to alter the thermoelectric cycle in a way which utilises the existing thermoelectric materials in favour of higher efficiency. On the other hand, the problem of the high cost of fabrication could be solved, by adopting new techniques, and this has been a much more fruitful area of research to follow.

A tape casting technique, was identified and em-

ployed as a fabrication process for the thermoelectric modules. This process is characterised by its simplicity and continuity, as well as, the low capital investment in its production equipment. These conditions were necessary to bring down the fabrication cost of the modules.

The fabrication cost of any generator, is dependent on the inter-connection technology and the methods of assembly. The tape casting process represents a departure from the expensive conventional techniques, of single-crystal, poly-crystal and the hot-pressed powder methods. These techniques tend to rely on the old methods of the electronic industries, where each layer is fabricated separately, and assembled later. These methods are characterised as skilled and labour-intensive, with labour costs approaching 80–90% of the total cost of the manufactured product. In the tape casting process, the flexible tapes are made into rolls, then shaped, cut and laminated on a belt-to-belt basis. The tape casting method is a semi-automatic process, requiring only a small non-skilled labour force. Also the capital investment in the tape casting equipment is

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small, since the equipment is already available and in use extensively in the ceramic and electronic industries.

2. Experimental procedure

2.1. Iron disilicide thermoelectric powder production

Iron disilicide (FeSi_2) powder samples were prepared from alloying elemental powders of silicon and iron, both of –325 mesh size and 99.9% pure obtained from Johnson Matthey (UK).

The elemental powders were first weighed accurately to the atomic ratio of FeSi_2 , under a protective gas of pure argon in a glove box. The powder with tool steel grinding balls are then placed inside two vials made out of hardened tool steel of 98-mm inside diameter. Finally the vials were sealed under argon, and then transported to the Fritsch planetary mill, model (PM5/2).

An alloying time of 30 h was considered as a sufficient time for producing FeSi_2 powder suitable for the tape casting process. The alloying time was achieved with the planetary mill rotating at 300 rev. min^{-1} , with 49 balls of 10-mm diameter per pot [1].

2.2. Fabrication of green tape by the tape casting process

A mixture of solvents (trichloroethylene/ethanol), FeSi_2 powder and a dispersant (glycerol trioleate) was sonicated first for 10 min using an ultrasonic probe (Soniprobe automatic type 7532A, DAWE Inst. Ltd). This procedure helped in breaking most of the agglomerates in the powder, reducing it to its original average particle size of 3.15 μm . Poly-methyl methacrylate (PMMA) binder, obtained from Rohm and Hass (US) under the commercial name of Acryloid B67, was then added to the mixture. The mixing was carried out in a closed polythene jar, with a flat 'T' shape blade, to minimise the creation of air bubbles within the slurry. A plasticizer (dibutyl phthalate), obtained from BASF, UK under the name of 'Palational C' was then added after 1 h and the mixture was left to homogenise for an additional 20 h.

After the mixing and the homogenisation of the slurry was completed, the slurry was de-aired. This process, was carried in a polythene jar containing slurry. The jar was evacuated using a vacuum pump set to a pressure of 200 mbar absolute for 3 min.

After the de-airing process, the slurry was cast on a casting surface or substrate. This was either glass, polythene or PTFE. The casting unit has two casting blades, to control the slurry flow onto the casting surface or substrate. The casting blades can be adjusted vertically with a pair of screws on the sides of each blade. Casting speeds were varied by a steppmotor

control drive board, up to a maximum casting speed of 40 cm min^{-1} . Drying the tape in still air was found to be detrimental to the surface texture of the tape, because of the formation of pools of solvent on the surface and as a consequence uneven shrinkage occurred. This problem was prevented by a slow airflow over the surface of the cast tape. The flow velocity should be not be so fast as to cause skinning, an airflow rate of less than 0.4 ms^{-1} was found ideal for the ethanol/trichloroethylene mixture. The air temperature was kept at 50°C, well below the ignition point of 71°C of the solvent mixture. The direction of the air flow was opposite to the casting direction of the tape, hence the vertical gradients in the solvent concentration was reduced, guaranteeing a continuously drying rate in the tape [2]. N- and P-type thermoelectric materials and ceramic green tapes, were all produced by this technique.

2.3. Thermoelectric generator fabrication and material criteria

The fabrication of the thermoelectric generator was carried out by stacking alternative N- and P-type FeSi_2 layers separated by shorter ceramic green tapes as shown in Fig. 1a. Upon pressing the structure, the areas of the N- and P-type materials, which were not separated by ceramic insulation, fuse together, effectively forming a hot and a cold junction alternatively, as shown in Fig. 1b.

Once the laminated multi-layer structure is sintered, a suitable electrical contact material of a low electrical resistivity can be applied to the two sides of the cold junction by an electro-plating technique. The final step of the generator fabrication is then carried out by soldering copper wires to the electrical contact, as shown in Fig. 1c,d.

The application of the electrical contact by electro-plating, is a well-established method, which can be carried out with no technical difficulties. The technical challenge in this fabrication technique lies mainly with finding a ceramic material compatible with the FeSi_2 semiconductor. Such a ceramic material, needs to possess two main criteria to successfully create a stable generator structure free of cracks and having good mechanical and electrical properties. These criteria are

1. The ceramic material should be sintered at the same temperature and time as the FeSi_2 (m.p. 1493 K).
2. The ceramic should possess a similar thermal expansion coefficient as the FeSi_2 material in the region of $10-12 \times 10^{-6} \text{ K}^{-1}$.

Other favourable criteria additional to those above are low-cost, high electrical resistivity, good mechanical

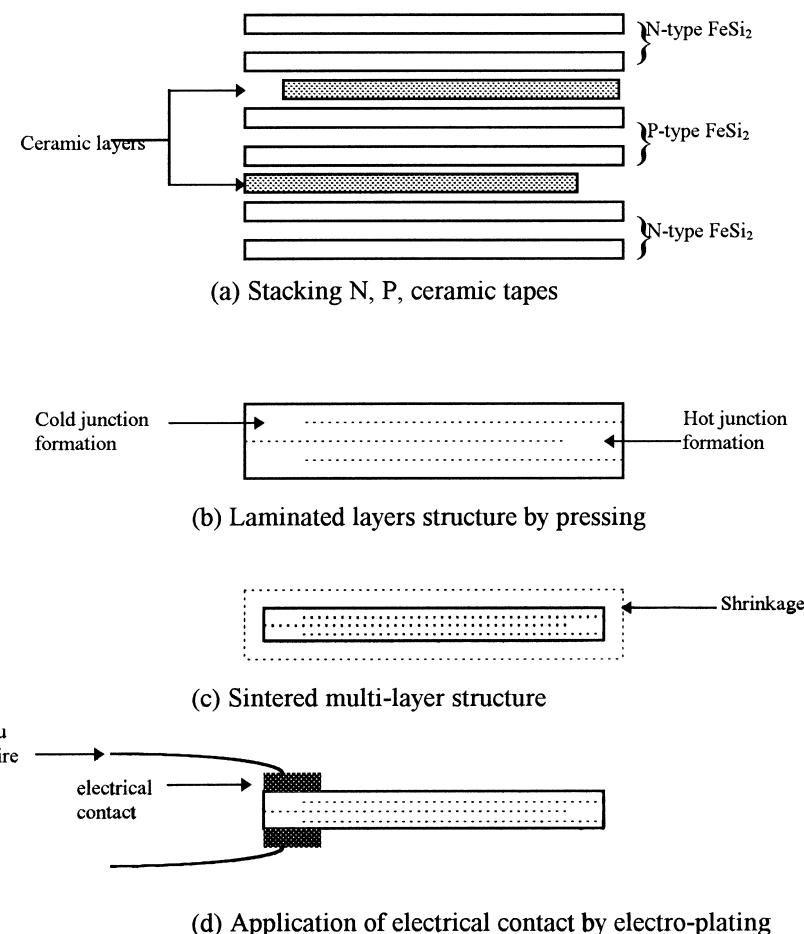


Fig. 1. Steps for fabricating an FeSi_2 thermoelectric generator from cast green tapes.

properties and material stability at the generator operating temperature range of 600–800°C.

2.4. Selected ceramics for the FeSi_2 generator

A search for ceramic materials compatible with the FeSi_2 material was conducted over large sets of alloy data from different ceramic properties sources [3–6]. It was apparent, that it would be very difficult to find a matching ceramic material, unless some relaxation of

the selection criteria could be made. Such a relaxation for instance could allow for a low density sintered ceramic due to a higher melting point than the FeSi_2 . Even with such a relaxation, the ceramic material must still achieve a high electrical resistivity and satisfactory hardness without having to compromise the effectiveness and the mechanical integrity of the generator.

Table 1 shows the properties of the ceramic materials identified as candidates for use with the FeSi_2 generator. The basis for the selection was either a

Table 1
Melting temperatures and thermal expansion coefficients of different ceramic alloys [3–6]

Ceramic formula of selected compounds	Melting point range (°C)	Thermal expansion coefficient $\times 10^{-6} \text{ K}^{-1}$ at different temperatures		
		500°C	1000°C	1500°C
$\text{BaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$	1227	9	–	–
$\text{K}_2\text{O}-\text{N}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$	1200	10	–	–
$\text{K}_2\text{O}-\text{BaO}-\text{SiO}_2$	1200	8	9	9.5
$\text{FeO}-\text{SiO}_2-\text{ZrO}_2$	1220	10	11	11
$\text{MgO}-\text{SiO}_2$	1550	10	11	12
$\text{MgO}-\text{Y}_2\text{O}_3-\text{ZrO}_2$	1700	9–10	11	13
$\text{MgO}-\text{CaO}-\text{ZrO}_2$	1700	10	11	12–13
$\text{MnO}-\text{MgO}-\text{ZrO}_2$	1220	8.9	–	–

matching sintering temperature or thermal expansion coefficient of the FeSi_2 material. Note, for some of the materials the thermal expansion coefficient are not quoted in the table due to a lack of published data of different ceramic alloys [3–6].

2.5. Pyrolysis, sintering and annealing of the laminated thermoelectric generator

Several thermoelectric generators comprising of N- and P-type layers of FeSi_2 green tapes and the different ceramic material types shown in Table 1, were fabricated to assess their compatibility with the FeSi_2 material. These tapes were laminated at a pressure of 200 MPa at 323 K for 5 min.

The procedure for the organic pyrolysis was analysed using differential thermal analysis (DTA), thermogravimetric analysis (TGA) and Fourier transformer infrared spectroscopy (FTIR). These analysis have been used to optimise the organic pyrolysis in term of heating rate of the tapes, atmosphere used and hold out time at the pyrolysis maximum temperature. Binder degradation mechanisms were constructed from the results of these analysis.

The pyrolysis procedures were carried out on the laminated green tapes using a horizontal furnace under different atmospheres. The complete organic burn-out was achieved at a pyrolysis temperature of 410°C, with an air flow rate of 1.2 l min⁻¹ and a hold out time of 2 h [7,8].

The sintering procedure was then carried out in a vacuum of 0.05 torr (6.5×10^{-5} atm) at 1473 K for 8 h, followed by annealing at 1093 K for 20 h. The ceramic alloy Mg_2SiO_4 was found to be the best material for compatibility with FeSi_2 matching the thermal expansion coefficient and the mechanical strength for the multi-layer generator.

The electrical contact for the generator was nickel electrode deposited on the FeSi_2 surface by electroplating, after which copper wires were soldered directly to the nickel electrode. The solder was either lead–tin (Pb/Sn, 60:40) with a melting point of 183°C, or zinc-based solder $\text{Zn}_{90}\text{Al}_5\text{Cu}_5$ (m.p. $\cong 380^\circ\text{C}$) [9].

3. Results and discussion

The sintering of the thermoelectric generator was carried out in vacuum at 1473 K, and a high density of 94.2% of the theoretical density of the FeSi_2 material was obtained. This high sintering temperature transforms most of the semiconducting β - FeSi_2 material into a metallic phase.

The high temperature metallic phase of the iron disilicide, consists of a cubic ε -phase and tetragonal α -phase. The ε -phase is an iron monosilicide FeSi , and

the α -phase exists within a wide composition range, being represented by the chemical formula Fe_2Si_5 .

The metallic phases of iron disilicide, possess poor thermoelectric properties with a Seebeck coefficient between 2.6 and 3 $\mu\text{V K}^{-1}$ and low electrical resistivities of 2.2 $\mu\Omega \text{ m}^{-1}$. The low temperature semiconducting phase, β - FeSi_2 , on the other hand possesses a large Seebeck coefficient of 250 $\mu\text{V K}^{-1}$ and an electrical resistivity of 1 $\text{m}\Omega \text{ m}^{-1}$. FeSi_2 undergoes a phase transition from a high temperature metallic structure to a low temperature semiconducting phase at or below 1223 K. Thus once the tape samples have been sintered, an annealing procedure below 1223 K was carried out to obtain a semiconducting phase with good thermoelectric properties.

Since the Seebeck coefficient α and the electrical resistivity ρ of the iron disilicide varies as the transformation takes place from a metallic to a semiconducting phase, the measurement of properties for the annealed tape at different temperatures, could be used as an indicator for such a transformation. These properties were measured at room temperature, with a 2–5-K temperature difference across the sample, using the measurement device described by Wynsberghe [10]. Room temperature measurements were found to be a sufficient indicator of the start and the end of the phase transformation within the material.

Sintered samples of N-type $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ with different doping level, $x = 0.02$ and 0.05, were annealed in the temperature range of 1073–1123 K, in order to determine the effect of the doping level, annealing temperatures and times on the Seebeck coefficient and the electrical resistivity of the samples.

Figs. 2 and 3 show the Seebeck coefficient and the electrical resistivity values for different samples annealed at 1093 K, for different durations up to 50 h. From these figures, it was clear that a minimum of 20 h annealing time was required to reach the saturation values of α and ρ of the semiconducting β -phase.

In order to determine the optimum annealing tem-

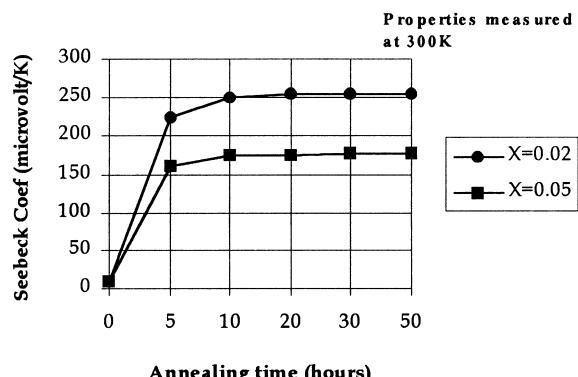


Fig. 2. Dependence of the Seebeck coefficient on the isothermal annealing time at 1093 K for $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ where $x = 0.02$ and 0.05.

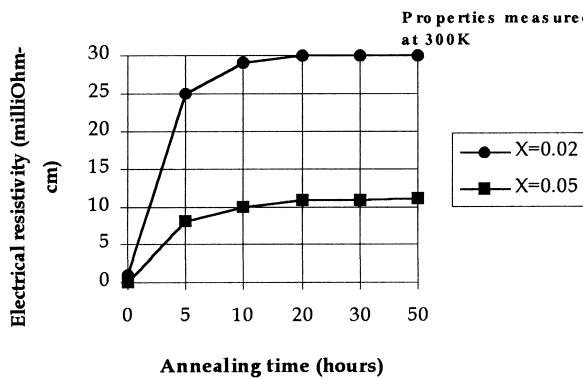


Fig. 3. Dependence of the electrical resistivity on isothermal annealing time at 1093 K for $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ where $x = 0.02$ and 0.05.

perature for the thermoelectric tapes, samples were annealed for 10 h at different temperatures. Their Seebeck coefficient and the electrical resistivity values are shown in Figs. 4 and 5, respectively.

The two figures confirm, that the transformation rate from a metallic to a semiconducting phase slows down as the temperature increases above 1093 K. The slow rate of transformation is indicated by the low values of the Seebeck coefficient and the electrical resistivity

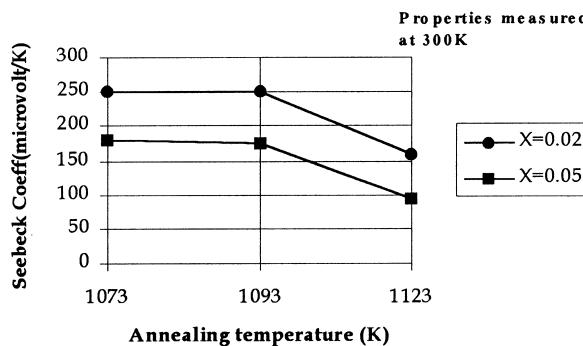


Fig. 4. Dependence of the Seebeck coefficient on isochronal annealing temperature of $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ with $x = 0.02$ and 0.5. Annealing time 10 h.

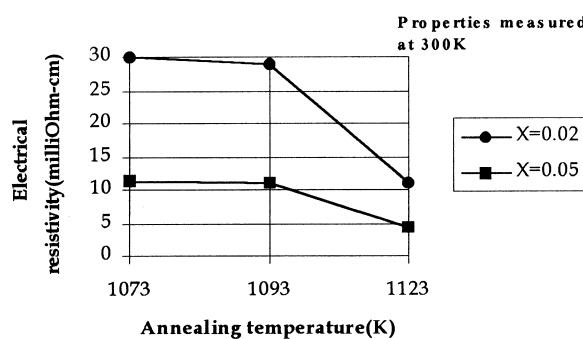


Fig. 5. Dependence of the electrical resistivity on isochronal annealing temperature of $\text{Fe}_{1-x}\text{Co}_x\text{Si}_2$ with $x = 0.02$ and 0.5. Annealing time 10 h.

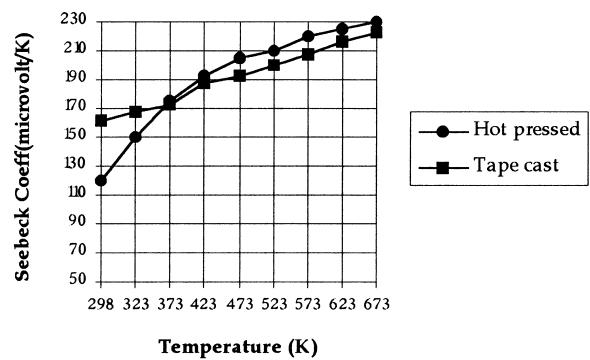


Fig. 6. Comparison of Seebeck coefficient of $\text{Fe}_{0.95}\text{Co}_{0.05}\text{Si}_2$ made by the tape casting and the hot pressing technique [11].

observed by annealing the sample at 1123 K compared to those annealed at 1093 or below for 10 h. On the other hand, only slight increases in the values of α and ρ were observed at 1073 K compared to those samples annealed at 1093 K.

In order to assess the performance of a thermoelectric generator fabricated by the tape casting, the thermoelectric properties of individual annealed tapes were measured up to 673 K. These properties could be then compared to the properties of materials made by the hot pressing technique [11–13]. Figs. 6 and 7 show a comparison of the Seebeck coefficient of the N-type $\text{Fe}_{0.95}\text{Co}_{0.05}\text{Si}_2$ and the P-type $\text{Fe}_{0.95}\text{Mn}_{0.05}\text{Si}_2$ made by the tape casting method with those made by the conventional hot pressing technique. Usually the hot-pressed materials possess the best thermoelectric properties of all other materials made by other techniques like cold pressing and ingot casting.

Figs. 8 and 9 show a comparison of the electrical resistivity values for the cast tape and the hot-pressed samples for the same materials as above.

These figures show that the Seebeck coefficient and the electrical resistivity values for the tape cast are lower than those of the hot press.

Unfortunately the thermal conductivity measure-

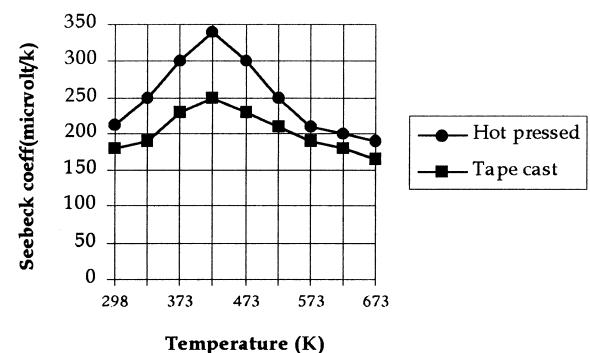


Fig. 7. Comparison of Seebeck coefficient of $\text{Fe}_{0.95}\text{Mn}_{0.05}\text{Si}_2$ made by the tape casting and the hot pressing technique [11].

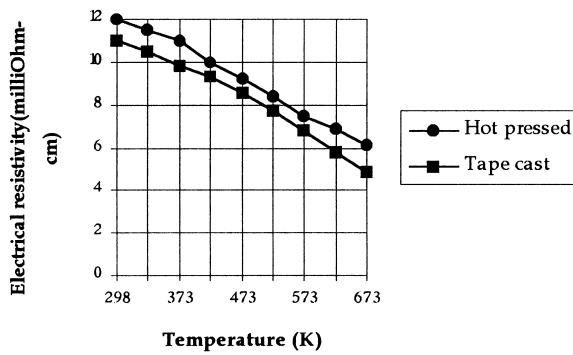


Fig. 8. Comparison of electrical resistivity of $\text{Fe}_{0.95}\text{Co}_{0.05}\text{Si}_2$ made by the tape casting and the hot pressing technique [11].

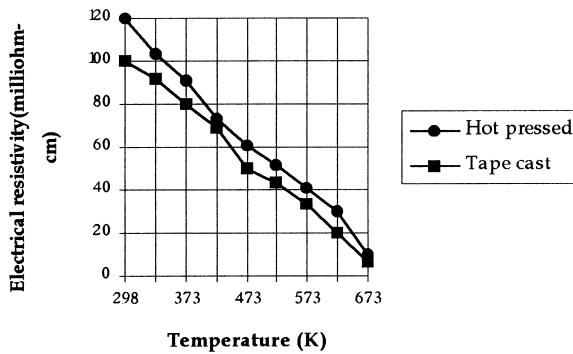


Fig. 9. Comparison of electrical resistivity of $\text{Fe}_{0.95}\text{Mn}_{0.05}\text{Si}_2$ made by the tape casting and the hot pressing technique [11].

ment was not accurate, but if the thermal conductivity of the tape cast and hot-pressed samples are assumed to be the same, 0.04 and $0.12 \text{ W cm}^{-1} \text{ K}^{-1}$ at 300 K for the $\text{Fe}_{0.95}\text{Co}_{0.05}\text{Si}_2$ and $\text{Fe}_{0.95}\text{Mn}_{0.05}\text{Si}_2$, respectively. Then the calculated figure of merit Z , for the tape cast samples would be 0.589×10^{-4} and $0.27 \times 10^{-5} \text{ K}^{-1}$, compared to Z of the hot press samples of 0.678×10^{-4} and $0.315 \times 10^{-5} \text{ K}^{-1}$, respectively. Therefore the best conventional technique of hot pressing produces better performance materials, than the tape cast materials by 13 and 14% for the cobalt and manganese-doped FeSi_2 , respectively.

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